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Porous Filter Element And Method
Of Fabrication Thereof

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The present invention relates to a porous filter element and in particular to a
5 method of manufacturing such a filter element.

There are many different types of porous filter element, ranging from the
relatively unsophisticated and familiar filter papers, and filters made of felt and
woven materials, to more sophisticated filters formed from, for example, porous
films, such as nucleopore filters and Anotech filters (made from an aluminum oxide
10 film).

Nucleopore filters are made by bombarding a polymer film with alpha
particles and then etching the regions damaged by the alpha particles to produce
holes. Because the pattern of holes is random, the intensity of alpha particles has to
be kept low to avoid holes running into each other. Thus the filter produced can only
15 have a low porosity if hole uniformity is to be maintained.

The present invention is concerned with a new way of making a porous filter
element, which gives close control over the shape and arrangement of the pores, and
which is capable of making a filter with a highly regular and controllable array of
pores over a large range of scales down to the microscopic.

20 In the present invention this is achieved by using a photosensitive material,
such as a photosensitive resin, as the starting material, and exposing this starting
material to an interference pattern of electromagnetic radiation so that different areas
of the photosensitive material are exposed differently according to the variation in
intensity caused by the interference. The material is then treated, e.g. using a
25 chemical solvent, to remove selectively regions which have been exposed by an
amount which is greater or less than a predetermined critical amount, this treatment
leaving voids in the material. The material can then be used either directly as a filter
element, or it can be used as a mould to produce a filter element, for instance by
filling the voids with a material which solidifies, and then removing the original
30 photosensitive material.

Because the array of pores is defined by the interference pattern of e.m.

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radiation, e.g. u.v. light, controlling this pattern gives close control over the shape, size and disposition of the pores. Interference patterns are highly regular and so a highly regular array of pores can be created.

The interference pattern can be created as a 3-D pattern in the photosensitive
5 material by interfering three or more coherent or partially coherent laser beams
therein. The pattern can be arranged to vary only in two dimensions, with it being
substantially constant in the third dimension (which may correspond to the normal to
the surface of the filter), so that the result of selective removal of material is an array
10 of constant cross-section channels extending through the material from one side of
the material to the other. Alternatively, it is possible to arrange for the interference
pattern to vary in the third dimension also by use of at least four interfering beams,
creating a pattern of interconnecting voids in the material which varies in all three
dimensions.

An alternative method for producing an interference pattern that varies in two
15 dimensions and does not require a coherent light source is a grating interferometer,
for example as described by Berger and co-workers [J. Appl. Phys. vol. 82, p.60-64
(1997)]. Alternatively, a pattern of exposure that varies in two dimensions may be
created by superposition of two or more exposures that vary periodically in intensity
in one dimension, but have different orientations.

For a given wavelength of e.m. radiation, the angles between the interfering
beams decide, and can be used to control, the period of the interference pattern. The
overall intensity of the interfering beams or the exposure time or the chemical
composition of the photo resist can be changed to change the pore size by varying the
amount of material which is exposed by more than the critical amount (and thus the
25 amount which is removed in the treatment step). Thus for a fixed periodicity the
pore size is continuously variable.

The relative polarization and relative intensity of the interfering beams can be
varied to adjust the shape of the pores by varying the pattern of interference.

Thus this close control of pore size and shape, with absolutely regular
30 periodicity, allows the pores to be packed very closely together and sized to make a
high throughput yet fine filter without the problem of pores joining together found in
a random creation process.

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Of course, in practice the interference pattern may only be created in a part of the body of photosensitive material. The rest can be used as an integral support or the porous part of the body can be cut out for use as a filter element.

Depending on the nature of the photosensitive material used, it is possible
5 that either regions which are subject to an exposure greater than a predetermined amount, or less than a predetermined amount, are removed by the treatment step. For instance, the material could be a resin in which cross-linking occurs on exposure to light, with non-cross-linked regions then being removed by using a suitable solvent, to create pores corresponding to the dark regions of the pattern.

10 The resin can contain a photosensitive agent which responds to the light and then causes cross-linking to occur either straightaway or on application of heat. In this way the pattern forms a "latent image" in the resin, which is developed subsequently by heating and chemical treatment.

15 Alternatively the photosensitive material can be one in which the exposure to light increases its solubility (either directly or via a photosensitive agent) by, for example, reducing the degree of cross-linking or by changing its polarity, in which case the pores will correspond to the light regions of the pattern.

20 The photosensitive material may conveniently be prepared in the form of a thin film (e.g. by spinning or spreading using a roller or blade), which is then exposed to the interference pattern.

25 Where the exposed and treated photosensitive material is to be used as a mould to form a filter element, the voids in the material can be filled with an inert material such as a metal, e.g. nickel, silver or gold, (which can be introduced by electrochemical or electroless deposition) or a ceramic, the photosensitive material then being removed. Where a ceramic is used, which is solidified by sintering, the sintering process is also effective to burn off the original photosensitive material.

30 The invention is capable of producing porous filter elements in which the pores consist of very long narrow channels through the element. For instance, the channels can have a diameter of the order of 0.1 micrometers, with a spacing of the order of 0.5 micrometers, in a filter element of thickness of the order of 30 micrometers. On the other hand, the same method is also capable of producing much

larger scale filters with regular arrays of pores over a large area.

The invention will be further described by way of non-limitative example with reference to the accompanying drawings in which:-

5 Figure 1 schematically illustrates the arrangement used to expose the photosensitive material;

Figure 2 schematically illustrates a first filter element according to the invention;

Figure 3 illustrates a second filter element made according to the invention;

10 Figure 4 is a scanning electron micrograph of a filter element of the type illustrated in Figure 2; and

Figure 5 is a scanning electron micrograph which shows the element of Figure 4 fractured; and

Figure 6 shows a simulation of an element with circular channels.

15 Figure 1 schematically illustrates the arrangement for exposing a body 1 of photosensitive material to a desired light pattern. As will be explained below, the body 1 of photosensitive material can be in the form of a spun film. In Figure 1 the light pattern is illustrated as being created by interference pattern of three laser beams 3, 5 and 7. It will be appreciated that in this arrangement, in which the angles between the light beams are determined by mirrors and not by diffraction from a grating, the beams need to be coherent or partially coherent and conveniently this can be achieved by beam splitting from a single laser source. This allows easy control of the overall intensity, e.g. by positioning crossed-polarizers before the beam splitter, and the intensity, polarization and angle of incidence of each beam is also adjustable using standard optical elements. As shown in Figure 1 the beams come together in 20 the body of photosensitive material to create in the material an interference pattern, which consists of a pattern of spatially varying intensity, in region 9. Thus the exposure (or radiation dosage) of the material in this region varies spatially.

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The use of three beams creates an interference pattern which varies in two orthogonal directions within the material, but not in the third orthogonal direction. Thus regions of constant exposure can be made to extend linearly through the depth of the material in a direction which connects one side to the other. Usually this

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direction will be perpendicular to the plane of the film, but it may also be slanted with respect to the perpendicular, should this be advantageous.

After sufficient exposure the exposed photosensitive material is treated, for instance by chemical development, to selectively remove regions of the material in dependence upon their exposure. Where, as explained below, the photosensitive material is a resin which cross-links in response to a certain exposure to light, the chemical development consists of removing using a solvent those regions which have not received a sufficient exposure to cross-link sufficiently (i.e. corresponding to the dark regions in the interference pattern). Although the intensity in an interference pattern varies smoothly, the response of the photosensitive material is non-linear so, the division between those parts of the material which have received a sufficient dose, and those which have not, is sharper than the variation in intensity of the interference pattern. Thus the effect of chemical development is to produce clearly defined voids in the material.

The necessary dosage of radiation can be applied either in a single exposure or in more than one exposure. The use of multiple exposure can increase the variety of structures which can be produced because the structure will correspond to a combination of different interference patterns, rather than to a single interference pattern.

Of course the region 9 in which interference occurs will generally be only a part of the prepared body of material 1. After chemical development this region may be cut-out and used. Alternatively the surrounding region can be uniformly exposed (or not) to create an integral support for the porous region.

The photosensitive material may be one which possesses an average number of crosslinkable groups per molecule of at least 3.0 with an equivalent weight per crosslinkable group of at most 1000. It has been found that with high functionality the network of crosslinks formed is potentially very dense giving high solubility contrast between strongly and weakly exposed material.

In general the photosensitive materials used in this invention are those possessing an average number of crosslinkable groups per molecule of at least 4, preferably at least 6 and especially about 8. They have an equivalent weight per

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crosslinkable group (XEW) in general at most 500, typically at most 400, preferably at most 300, especially at most 230. Suitable photosensitive materials which can be used include epoxy resins ie. epoxy groups act as the crosslinkable groups.

It has been found that it is particularly advantageous to use the glycidyl ether of bisphenol A novolac which is available as EPON-SU-8 from Shell Chemicals.
5 This resin has low intrinsic absorption at the laser wavelength ($\lambda = 355$ nm) and is capable of sub 0.1 micron resolution. It has an average of 8 epoxy groups per molecule. The material is therefore mostly in the form of a tetramer although other oligomers will usually be present. Its XEW is generally about 215, with a typical
10 range from 190 to 230. It may be desirable to co-polymerise this material with a less crosslinkable plasticising epoxy monomer e.g. one with a single epoxy group in order to minimise shrinkage and/or film distortion on heating of the material (thereby reducing the functionality somewhat). Alternatively, the resin can be modified by using a so-called "expanding" monomer such as a spiro-orthocarbonate.
15 Alternatively, improved physical properties of the polymer can be obtained by the addition of a binding agent such as a linear polymer. Effectively, any polymer can be used provided that it has sufficiently high functionality and the precursors have a low degree of optical absorption at the laser wavelength within a film typically 10-100 microns thick.

20 In one preferred embodiment of the present invention the photosensitive material is subjected to irradiation in the presence of a photo acid generator. Subsequent to exposure the material is heated to cure the crosslinked material.

Suitable photoacid generators which can be used, especially with epoxy resins, include onium salts such as triaryl sulfonium salts including triphenyl
25 sulfonium antimony chloride which is available as CyraCure UV1 from Union Carbide. This particular generator is well suited to irradiation at 355 nm where it has sufficient absorption (molar extinction coefficient $\sim 300 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$). In general the molar extinction coefficient of the PAG should be from $50 - 2000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ at the laser wavelength. If the molecular coefficient is too large, the requirement for the sample to be optically thin means that the concentration of initiators is too small
30 to effect polymerisation. On the other hand if it is too small, the PAG concentration

is so high that it adversely affect the properties of the polymer. By "optically thin" is meant that at the concentration at which it is used the PAG does not absorb more than 5% of the radiation which is incident upon it. In addition the quantum efficiency of the PAG should be sufficient for the exposure to cause insolubilisation of the photosensitive material. The effective quantum efficiency will be enhanced if the system involves chemical amplification. Obviously sufficient photosensitive material must be insolubilised to provide a volume of insolubilised material which is useful for practical purposes i.e. a useful volume, for example 1 mm³ e.g. a film of size 5 x 5 x 0.04 mm. By "cause insolubilisation" is meant that there is sufficient proton generation for subsequent acid catalysed polymerisation, as discussed below, to result in a crosslinked material which is insoluble in a solvent which dissolves the unirradiated or weakly irradiated material. One of skill in the art will, of course, be able to select an appropriate PAG from those possessing the required molar extinction coefficients and optical thinness. For SU-8 a quantum efficiency of about 0.2 is needed for proton generation in the PAG. It is believed that the insolubility threshold is reached when each absorbed photon leads to the conversion of material equivalent to about 250 or 500 crosslinkable groups, for example about 600 epoxy groups, into insoluble polymer.

A specific example of the materials and process used to produce a filter element (actually the one shown in Figures 4 and 5) will now be described.

The photosensitive material was prepared by dissolving Epon-SU8 resin (Shell Chemicals), the glycidyl ether of bisphenol-A novolac, in γ -butyrolactone (50-60% wt. solids) with gentle heating (~30-40°C) and manual stirring. The resulting viscous solution was filtered to exclude particles larger than 1 μm . Between 0.5% wt. and 3% wt. of a photoacid generator (PAG), a triaryl sulfonium salt (Cyracure UVI from Union Carbide) was added to the solution. The amount of PAG added determines the sensitivity of the photoresist, with 1.2% giving good results for these experimental conditions. The resulting photoresist was mixed thoroughly (and can be stored in the dark and away from heat sources until required).

Solid films of the photoresist (2-30 μm for the 50% wt. resist and 10-60 μm for the 60% wt. resist) were prepared by spinning the resist onto fused silica disks

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(~2 cm diameter). For example to prepare a ~30 μm film, approx. 2 ml of the photoresist is pipetted onto the disk so that it is flooded. The film is then spun at 1000 rpm (5s ramp up, 40s hold, 5s ramp down) and then undergoes a post application bake (PAB) at 50°C for 5 mins followed by 15 mins at 90-100°C to 5 evaporate the solvent. The interval between film preparation and exposure is kept as short as possible and generally less than 30 mins. Films can also be prepared by spreading, moulding or pouring.

The film was then exposed to an interference pattern created at the intersection of three beams from a frequency-tripled, injection seeded, Q-switched 10 Nd:Yag laser (wavelength $\lambda=355$ nm). Such a pattern has two dimensional periodic translational symmetry.

The propagation directions, polarisation directions and relative intensities used are defined as follows:-

Normalised optical wave-vectors (relative to the conventional fcc unit cell 15 axes):

(1)	-0.96225038	-0.19245008	-0.19245008
(2)	-0.19245008	-0.96225038	-0.19245008
(3)	-0.19245008	-0.19245008	-0.96225038

Polarisation unit vectors (in the same frame):

20	(1)	0.269517	-0.575382	-0.772202
	(2)	0.804841	-0.0425761	-0.591961
	(3)	0.933817	-0.337270	-0.119310

Relative intensities ($I_1:I_2:I_3$); (1:1:1)

These polarizations and relative intensities create essentially triangular 25 channels (though with rounded corners). Varying the polarizations and relative intensities can create circular or elliptical channels, or other shapes as desired.

For instance circular channels as shown in Figure 6 can be created by using the following polarisation vectors:-

30	(1)	0.0000000	-0.7071068	0.7071068
	(2)	0.7071068	0.0000000	-0.7071068
	(3)	-0.7071068	0.7071068	0.0000000

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The films were exposed in a single pulse (6 ns) of the laser. The total dose can be varied from 80-200mJcm⁻² depending on the required polymer/air ratio in the filter. (The filling factor is also related to the time and temperature of the post exposure bake). The glass substrate was index matched to a thick glass block using mineral oil in order to reduce back reflections.

The beam geometries described above are those required to define the appropriate interference pattern in air. In practice refraction occurs as the beam enters the film of resist but it is possible to compensate for the refraction by changing the angle of the beams. This can be done, for example, by adding a shaped transparent optical element or elements with refractive index greater than unity into the beam paths, and may include the use of high index liquid between rigid optical elements.

The pulse duration is not critical. With an injection seeded laser the coherence length is equal to the pulse length, but this requirement can be relaxed if the optical path-lengths are made accurately equal. A cheaper but less effective option for increasing the coherence length is etalon-narrowing. In practice it is only necessary to achieve a coherence length of ~1cm. An ordinary un-narrowed Q-Switched Nd-YAG laser can approach this requirement. More importantly though injection-seeding makes the pulse energies, following third harmonic generation, far more reproducible, so that the control of the dose in a single pulse exposure becomes straightforward. A further advantage of single pulse operation is the absence of significant refractive index changes, that could perturb the interference, during the exposure.

Alternative light sources can be used, providing the photoinitiator is chosen to match the operating wavelength. An optical parametric oscillator or alternative laser which is continuously tunable, could therefore be used to construct filters with different spacings of pores, with or without a change in the angles between the interfering beams.

The exposure of the resist results in the production of a proton from the photochemically induced fragmentation of the PAG molecule. Acid catalysed polymerisation of the SU8 resin occurs in a post exposure bake (PEB). The glass

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substrate was placed directly on a level hotplate at 40-120°C for between 1-20 mins depending upon the exposure dose, % PAG in the resist and the required filling factor. An PEB temperature below the melting point of the SU8 resin (80-90°C) results in a much "cleaner" lattice than one produced with a PEB above the resin's melting point.

The film was then developed in propyl glycol methyl ether acetate (PGMEA) in an ultrasonic bath to dissolve away the uncrosslinked resin. During development the film becomes detached from the substrate. The ultrasonic power was damped or attenuated to ~7 W to avoid mechanical damage to the film as it releases from the substrate. The bath was thermostated at 40-50°C and a typical development time is 40 mins for a 30 µm film. After the bath development, the film was washed with fresh PGMEA and finally rinsed in isopropyl alcohol before drying in air.

The resulting porous element is illustrated schematically in Figure 2. The body of photosensitive material 1 has an array of parallel channels 13 extending from one side to the other. A scanning electron micrograph of the actual filter element produced by the above method is shown in Figure 4. It is shown at higher magnification and fractured in Figure 5, where the channels 13 can easily be seen. It will be noted that the array is very regular, and that the channels are extremely narrow compared to their length.

The above example creates uniform channels through the filter. It is possible though, to vary the shape of the channels with depth. A schematic illustration of such a filter element is shown in Figure 3. It can be seen that the channels have a narrow section 15 at one end, which communicates with a wider section 17. If this is used to filter material passing from top to bottom in the orientation illustrated in Figure 3, it is a "non-blocking" filter. This can be produced in several ways. For instance, the photosensitive material 1 can have two layers of differing compositions. The top layer, which will form the narrowed part of the channel, has more PAG than the lower layer, so more cross-linking occurs on exposure, thus resulting in narrowed holes.

Alternatively a different intensity of illumination can be created in the region desired to have narrow holes, for instance a greater intensity there can be achieved by

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uniformly exposing that surface with a shorter wavelength light which does not penetrate far into the photosensitive material, or with an evanescent wave whose field penetrates a short distance into the photosensitive material.

The filter element made using the techniques above can be supported for use
5 on a porous substrate having larger pores than the filter to provide a non-blocking arrangement. The substrate can be made by the same technique, or by one of the standard techniques for making filters.

It will be appreciated that the invention is not limited to the materials described in the above example. For instance other epoxies or other photosensitive
10 materials can be used, and as mentioned the process can be changed so that the degree of polymerisation/cross-linking in the material is higher in the regions of lower exposure to light, than it is in the regions of higher exposure to light. Thus both "negative" and "positive" processes are possible.

Further, although the above example uses a very fine interference pattern to
15 create a very fine filter, the method is equally applicable to much larger scales, simply by producing an interference pattern of the desired scale.

The porous element made by the above method can be used directly as a filter element. Alternatively the technique can be used to make a mould from which a filter element of another material is created. For instance, an element produced using
20 the materials above can have the voids filled with a ceramic such as titanium (IV) oxide and then be heated (e.g. to 575 °C) to burn off the resin mould and sinter the ceramic. As an alternative to using a ceramic the voids in the resin can be filled with a material which is insoluble in a solvent for the resin. The resin can then simply be dissolved away. Of course, it is necessary either that the voids in the element are
25 connected together so that the solidified filling will support itself when the resin is removed, or some other support must be provided for the solidified filling. It will be appreciated that the specific element produced by the method above and illustrated in Figure 4 would mould a disconnected array of upstanding "rods" which are not self-supporting. Connectivity can be achieved by varying the interference pattern so that the "rods" become connected (without losing porosity). Alternatively the "rods"
30 could be formed on a substrate which supports them.